

# Compression Molding of Phenolic Resin and Corn-based DDGS Blends

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**Abstract** With the rapid growth in the ethanol fuel industry in recent years, considerable research is being devoted to optimizing the use of processing coproducts, such as distillers dried grains with solubles (DDGS), in livestock diets. Because these residues contain high fiber levels, they may be amendable to incorporation into bio-based composites. Thus, the goal of this study was to demonstrate the viability of using corn-based DDGS as a biofiller with phenolic resin, in order to produce a novel biomaterial. DDGS was blended with phenolic resin at 0, 10, 25, 50, 75, and 90%, by weight, and then compression molded at 51 MPa (3.7 tons/in<sup>2</sup>) and 174 °C (345°F). Molded specimens were then tested for tensile strength. Tensile yield strengths ranged from 32 MPa (4,700 psi) to 7.6 MPa (1,100 psi), while the engineering strain ranged

from 0.6% to 1.25%. Results indicate that DDGS concentrations between 25% and 50% retained sufficient mechanical strength and thus represent reasonable inclusion values. Additionally, data were similar to those from other studies that have investigated biofillers. Follow-up studies should quantify the effects of altering molding parameters, including molding pressure, temperature, and time, as well as pretreatment of the DDGS. Additionally, strength of the DDGS composites should be optimized through the use of coupling agents or other additives.

**Keywords** Biofillers · Bioplastics · Composites · Mechanical Properties · Tensile Testing

## Introduction

Currently, many plastic products utilize low-cost materials as fillers. Fillers are commonly used with thermoset resins such as phenolics, ureas, and melamines [1]. Ideally the filler is added in a concentration that maintains mechanical strength, physical properties, and final quality at levels similar to that of the pure resin. If a filler has some fibrous structure, it may increase mechanical properties, such as impact resistance, in addition to providing bulk volume. Also, certain fillers may improve a plastic's other physical properties, such as flame retardance, thermal stability, color, and opacity. While a filler may improve a composite material's overall properties, it may in some cases actually degrade mechanical properties, such as tensile strength and ductility. As long as the filler is added in a reasonable quantity, any degradation in property performance may be offset by the cost savings. Common fillers include clay, talc, calcium carbonate, ground limestone, carbon black, marble dust, glass, paper, wood flour, and metals. Fillers

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are typically added in concentrations ranging from 10% to 50% (by weight). To conserve petroleum resources and enhance biodegradability, bio-based fillers are receiving increased attention. Examples include wood flour, sugar cane, lignin, flax, grasses, bamboo, starch, chicken feathers, soy protein, and cellulose, to name a few. Several reviews documenting the use of biofillers in various plastics are available in the literature [2–4].

Phenolic resins are produced by chemically combining phenols and formaldehyde through a condensation reaction under alkaline conditions. Depending on the specific reaction mechanism employed, either a resole resin or a novolak is formed. Resoles are referred to as single-stage polymers since they do not require any curing agent. Novolaks, on the other hand, are designed to incorporate a curing agent, such as hexamethylenetetramine (hexa), and are referred to as two-stage; fillers and additives are then added to produce standard phenolic molding compounds. Applications include castings from molding powders, coatings, adhesives, and as a binder. Phenolic resins can tolerate high temperatures and bear large mechanical loads with minimal creep and are also bonding agents, since they mix well with both inorganic as well as organic fillers and reinforcements. Additionally, the phenolic molecules cross-link through the fillers and reinforcements, which also helps to provide excellent final properties.

Dry milling and wet milling of corn to manufacture ethanol fuel produces large quantities of processing byproducts known as distillers grains. These materials are the non-fermentable residues left after the starch fraction of corn has been brewed with yeasts and enzymes to produce ethanol. The dry milling process is substantially simpler than wet milling and is thus more commonly used. Coproducts from dry milling include distillers dried grains (DDG), distillers dried grains with solubles (DDGS), condensed distillers solubles (CDS), and distillers wet grains (DWG), depending on specific drying and blending processes employed. These distillers grains, especially the DDG and DDGS, represent potentially viable biofillers especially because they contain a relatively high fiber content, sometimes even up to 50% (dry basis).

Although there are no data available in the open literature for the combination of phenolics with DDGS, phenolic molding compounds commonly use wood flour as a filler. In fact, wood flour is, perhaps, the oldest biofiller utilized in plastics. Wood is mostly composed of cellulose and lignin; these molecules have reactive sites and functional groups that readily bond with phenolics. Over the years, combinations of wood flour and phenolic resin have been investigated and optimized for mechanical strength and moldability. Biofillers are added to phenolics in two ways: chemical reaction and simple mechanical mixing.

### Chemically Reacted Fillers

Using a chemical reaction to combine filler and phenolic, prior to molding, leads to enhanced interfacial bonding between the materials when molded into a composite. For example, Maldas and Shiraishi [5] liquefied birch wood in phenol using sodium hydroxide (NaOH) as a catalyst. The mixture was heated to augment the chemical reaction, then cooled to form “phenolated wood,” and was mixed with wood flour and other additives to form a molding powder. Samples were compression molded at 38 MPa (2.8 tons/in<sup>2</sup>) and 190 °C (374°F) for 7 min. Flexural properties of molded specimens were obtained for varying wood-to-phenol ratios and NaOH concentrations. In general, greater phenol content in the phenolated wood yielded higher flexural strength, modulus, and toughness. But, in all cases, the mechanical properties of the phenolated wood/wood filler blends were sharply reduced when compared to specimens molded from a standard novolak. The strength was only 15–40% of the standard commercial novolak, while the flexural toughness decreased even more, to only 5–20% of the novolak value. The flexural modulus fared better, ranging from 1/3 to 2/3 of the novolak’s value. To improve this mechanical performance, the phenolated wood solution was modified by reacting it again, after cooling, to form a “resinified phenolated wood” [6]. As before, this material was mixed with wood flour and specimens were mechanically tested. A significant increase in performance was noted; compared to the standard novolak, the flexural strength was only 5–20% reduced, while the flexural modulus actually increased 25–35%. The toughness, although greatly improved, was still 30–50% lower than novolak-molded specimens. The improvements were attributed to higher levels of reacted phenol, which provided better interfacial adhesion between the phenolated wood and the wood flour filler.

Similarly, corn bran was liquefied, phenolated, and mixed with wood flour at various levels, along with other additives, to produce a molding compound [7]. Specimens were compression molded at 50 MPa (3.6 tons/in<sup>2</sup>) and 170–180 °C (338–356°F) for 1–30 min; the specimens were then tested for flexural strength. The mechanical performance of the corn bran-based material was comparable to phenolated wood as well as novolak resins.

Another biomaterial, lignin, in dry powder form, was reacted with phenolic resin, and samples were compression molded at 47 MPa (3.4 tons/in<sup>2</sup>) and 160 °C (320°F) [8]. Blends included 0, 15, and 30% lignin, where the 0% case represented pure phenolic resin (i.e., without any fillers). Specimens were tensile and Izod impact tested. Compared to the 0% lignin, results indicated a 20–30% reduction in tensile strength and a 10–15% decrease in impact strength as the lignin content increased from 15% to 30%.

Chemically combining a biofiller with phenolic resin, however, is a complex process compared to simply mixing the filler with phenolic powder to form a blend which can subsequently be molded by a heated, pressurized process, and any reactions that occur take place during the molding (i.e., curing) stage. Thus it behooves us to examine cases where biofiller is mechanically mixed with the phenolic.

#### Mechanically Blended Fillers

Kharade and Kale [8] studied a novolak-based molding compound which was produced by mixing phenolic, coconut shell powder, and other additives with wood flour and/or lignin; the inclusion levels of wood flour and lignin were systematically varied. Based on the total molding compound weight, wood flour/lignin percent ratios included 25.3/0 (no lignin), 15.3/10, 5.3/20.3 and 0/25.3 (no wood flour). Tensile strength and impact testing demonstrated greatly reduced performance as more lignin replaced the conventional wood flour. Tensile strength decreased sharply; at 0% wood flour (25.3% lignin) the decrease was 75%. Impact strength suffered similar decreases. In this case, the blended lignin reduced properties much more rapidly compared to the chemically phenolated lignin. It was suggested that perhaps the lignin produced a better bond when chemically reacted with the phenolic before molding, compared to simply adding it as a filler to replace wood flour in the molding compound.

Along the same lines, wood flour and lignin (from Alpha grass) were examined in a phenolic [9]. Alpha grass lignin or wood flour constituted 0, 5, 15, 25, 35, or 45% of the total mixture, with the remainder composed of phenolic and additives. Test specimens were molded at 20 MPa (1.5 tons/in<sup>2</sup>) and 170 °C (338°F) for 17 min. As more phenolic was displaced, the impact strength decreased at approximately the same rate for either lignin or wood flour. Compared to no lignin or wood flour, the impact strength decreased about 40 and 35% for 25% lignin and 25% wood flour, respectively. For 45% lignin or wood flour, the impact strength was about half the strength without any of these biofillers.

Dried sugar cane pulp fiber served as another biofiller in a phenolic, hexa, and calcium stearate mixture and was blended at 29 and 69% [10]. Also, two different cane grain size distributions were tested: 35 to 80 mesh, and 80 to 170 mesh. The molding conditions were 14.7 MPa (1.1 tons/in<sup>2</sup>) and 170°C (338°F) for 10–15 min. In both cases, the addition of the sugar cane residue raised tensile strength significantly. For example, the 35 to 80 mesh (which is more representative of typical wood flour grain size) yielded a 75% increase in tensile strength for the 29% cane pulp blend. The 69% pulp blend performed the same as the pure resin case, although it exhibited a 40%

better tensile strength at the 80 to 170 mesh level. It was postulated in this study that a higher level of cane fibers interfered with the phenolic wetting of the cane, which resulted in weaker fiber/matrix bonding. Although the cane apparently added significant strength to the phenolic, it should be noted that the pure phenolic resin was not particularly strong; its tensile strength was 16.4 MPa (2,380 psi). This may have allowed for a greater level of reinforcement from any filler.

The ethanol fuel industry is currently experiencing an exponential expansion in the U.S., and it is generating increasing quantities of high fiber DDGS. The objective of this study was to demonstrate the feasibility of using this material as a biofiller with phenolic resin to produce a novel biocomposite.

#### Materials and Methods

To determine the feasibility of blending DDGS with phenolic resin, strength properties were quantified. Concentration of DDGS was varied by weight (0, 10, 25, 50, 75, and 90% inclusion), each blend was compression molded, and the resultant mechanical properties were evaluated using standard tensile testing according to ASTM D638-03 [11]. Two runs of pure resin (0% DDGS) and one run each of the other DDGS blends, for a total of seven runs, were completed. The pure resin was processed twice to provide an estimate of the repeatability and variability of the data. Identical molding and testing procedures were followed for each test specimen.

#### Compression Mold for Tensile Bar Specimens

The main advantage of compression molding with biofillers, over other common processes such as injection molding and extrusion, is the minimal damage to the filler when combining with the resin melt during molding. The filler has a very short flow path; it simply compresses along with the resin during processing. Additionally, compression molding is a preferred method for processing thermoset resins, such as phenolics, polyesters, and epoxies, all of which may incorporate reinforcing fibers.

For this study, a tensile bar mold was fabricated to produce Type I test specimens according to ASTM D638-03. This compression mold (Fig. 1) was instrumented so that temperature and pressure data could be recorded. The mold consisted of two halves of a matched set. It was made from 4140 steel, which is a high strength, low-alloy material. The mass of the mold was 13.8 kg (30.5 lb<sub>m</sub>) and, when closed, measures 225 mm (8.875 in) in length, 58.8 mm (2.313 in) in width, and 88.9 mm (3.500 in) in height. To facilitate the removal of the molded specimens,

**Fig. 1** Tensile bar mold constructed for the study



an ejection system was designed and incorporated into the mold itself.

To instrument the mold with thermocouples and pressure sensors, insertion holes were added. The pressure sensor was located at the far end of the lower mold half; this location was chosen to prevent molding imperfections in the center portion of the tensile bars (i.e., the break region). One thermocouple was located in each half of the mold. The thermocouple probes were type J (iron-constantan) and were connected to a digital monitor. The pressure transducer had a range of 0–68.9 MPa (10,000 lb<sub>f</sub>/in<sup>2</sup>), contained a type J thermocouple at its tip, and was monitored via a digital readout. The data from this transducer were used to verify that the molding force was indeed transmitted to the resin blend in the mold cavity. Another pressure monitor, 0–34.5 MPa (5,000 lb<sub>f</sub>/in<sup>2</sup>), was used to read the hydraulic pressure of the compression molder. A rotary thermocouple selector switch was also used, which allowed the reading of all three mold temperature probes, as well as a fourth thermocouple for monitoring ambient temperature. The mold temperature was taken as the arithmetic mean of the three probe values. Temperature measurement uncertainty due to the readout was  $\pm 0.4$  °C ( $\pm 0.7$  °F), while the thermocouple probe uncertainty (standard type J limits of error) was  $\pm 2.2$  °C ( $\pm 4.0$  °F). The molder hydraulic pressure monitor, with its transducer, had an uncertainty of less than 0.09 MPa (13 lb<sub>f</sub>/in<sup>2</sup>). The entire system is shown in Fig. 2.

### Compression Molding

The phenol and formaldehyde resin was a commercial-grade powder of 91.5% phenolic with 8.5% curing agent (hexa) without any other additives or fillers as found in conventional molding compounds. The distillers dried grains with solubles (DDGS) were obtained from a commercial dry-grind ethanol plant in eastern South Dakota. Using standard AOAC methods, it was determined that the DDGS had a protein content of 27.6%, fiber content of 11.1%, fat content of 9.3%, ash content of 4.2%, and other carbohydrates of 47.8%; the percentages are on a dry basis.



**Fig. 2** Compression molding experimental facility

To produce the various blends, the phenolic powder was mixed with the appropriate quantities of DDGS in an 89 ml (3 oz) plastic cup and stirred for about 90 s to achieve a uniform blend. Each blend used 14 g (0.5 oz) as the charge for each tensile bar. Both mold halves were cleaned to remove any debris from previous runs, mold release wax was coated onto both halves of the mold, a tensile bar ejector blank was placed in the cavity, and the blended mixture was poured into the cavity. The upper and lower mold halves were matched and closed, and the entire mold was centered on the bottom platen of the 222-kN (25-ton) compression molder. This platen was raised by manually pumping the compression lever until the upper mold surface touched the top platen. Using the pump lever, the hydraulic pressure of the molder was then increased to 19.3 MPa (2,800 lb<sub>f</sub>/in<sup>2</sup>). With a specimen surface area of  $2.52 \times 10^{-3}$  m<sup>2</sup> (3.91 in<sup>2</sup>), this pressure equates to a compression force of 51 MPa (3.7 tons/in<sup>2</sup>) which is well within the recommended range of 13.8–68.9 MPa (1–5 tons/in<sup>2</sup>) for phenolics [1]. This study utilized DDGS in its raw, untreated form and because of the moisture content (12.3% dry weight basis), with perhaps other volatiles present, it was necessary to begin the process with the mold and platens at room temperature; this procedure is referred to as “cold molding.” Otherwise when starting



**Table 1** Sample molding parameters over entire molding cycle

Time (min)	Molding unit force MPa (tons/in <sup>2</sup> )	Upper platen temperature		Lower platen temperature		Mold temperature at pressure transducer		Mold temperature in lower half		Mold temperature in upper half	
		°C	(°F)	°C	(°F)	°C	(°F)	°C	(°F)	°C	(°F)
0	48.5 (3.52)	27	(80)	27	(80)	26	(79)	24	(76)	27	(80)
5	45.9 (3.33)	77	(170)	66	(150)	52	(126)	56	(133)	55	(131)
10	47.6 (3.45)	96	(205)	88	(190)	72	(162)	78	(172)	78	(172)
15	47.6 (3.45)	122	(252)	106	(223)	97	(206)	99	(211)	103	(218)
20	47.6 (3.45)	154	(310)	133	(272)	117	(243)	122	(252)	129	(264)
25	48.5 (3.52)	167	(332)	160	(320)	138	(280)	141	(286)	146	(295)
30	48.5 (3.52)	199	(390)	196	(385)	167	(333)	172	(342)	179	(354)
31	8.8 (0.64)	Platen heaters are turned off									
40	7.9 (0.58)	34	(93)	27	(80)	64	(147)	54	(130)	107	(225)

with heated platens, the volatiles would cause expansion of the mixture and premature curing, which would result in weak, porous, and not fully cured specimens. Thus the platen temperatures were slowly increased. Compression force, top and bottom platen temperatures, the three mold temperatures, and the ambient temperature were recorded every 5 min during processing. The process continued until the mold temperature reached approximately 174 °C (345°F); this required about 30 min. Table 1 contains a sample set of molding data over time.

The mold was cooled prior to specimen removal. During this time, the compression force was reduced to 8.8 MPa (0.64 tons/in<sup>2</sup>), the platen cooling circuit was activated, and cooling water was circulated for 10 min. This reduced the mold temperature to approximately 49 °C (120°F), at which point it could be safely removed from the mold. The mold halves were separated to remove the finished tensile bar specimen. The specimens were slightly sanded to remove excess flash and uneven edges, rinsed with water, dried, and placed in a constant temperature/humidity chamber for conditioning at 23 ± 2°C (73.4 ± 3.6°F) with 50 ± 5% relative humidity, for at least 40 h prior to tensile testing, following the prescribed procedure [11].

### Tensile Testing

Tensile bar width and thickness in the narrowed (i.e., break) region measured 12.7 mm (0.5 in) and 3.2 mm (0.125 in), respectively. Each specimen was clamped between the jaws of a 24.5-kN (5,500-lb<sub>f</sub>) tensile tester; the specimen distance between the jaws was 76 mm (3 in). Care was taken to properly position the specimen; a bubble-level indicator was used to ensure that each specimen was completely vertical. The tensile test was automatically performed, with 100 tensile force versus elongation data points measured. The specimen was pulled until failure (i.e., break). For all data points, the tensile force was divided by the initial cross-sectional area to obtain engineering stress while the elongation was divided by the initial length to determine engineering strain (%).

### Results and Discussion

The tensile yield strength, Young's modulus (i.e., slope of the stress–strain curve), and elongation at yield (%) are provided in Table 2. The data indicate that, in general,

**Table 2** Tensile test data for a molding pressure of 51 MPa (3.7 tons/in<sup>2</sup>), mold temperature of 174 °C (345°F), and molding time of 30 min

DDGS %	Engineering tensile yield strength MPa (psi)	Young's modulus MPa (psi)	Elongation at yield %
0	32.1 <sup>a</sup> (4,654) <sup>a</sup>	2,678 <sup>a</sup> (388,490) <sup>a</sup>	1.25 <sup>a</sup>
10	18.1 (2,630)	3,043 (441,311)	0.59
25	19.4 (2,809)	2,595 (376,344)	0.76
50	17.9 (2,598)	1,967 (285,305)	0.94
75	9.4 (1,370)	1,548 (224,563)	0.63
90	7.7 (1,116)	1,076 (156,104)	0.73

<sup>a</sup> Average of two runs at pure resin

mechanical properties decrease (as expected a priori) as the inclusion of DDGS filler increases. Tensile yield strengths ranged from 32 MPa (4,700 psi) to 7.6 MPa (1,100 psi), while the engineering strain ranged from 0.6% to 1.25%. It should be noted that the tensile yield and break values were identical, which was expected for brittle materials. The exception was the 90% DDGS sample, which seemed to exhibit a slight transition from the yield point (where the stress–strain curve deviated from linearity) to the break point. Other data exhibited rather linear stress–strain curves with yield and break occurring simultaneously. Young's modulus ranged from 3,034 MPa (440,000 psi) for 10% DDGS to 1,034 MPa (150,000 psi) for 90% DDGS.

A more meaningful presentation of the data can be seen by the ratio of a given mechanical property value for any DDGS blend, divided by the value of that property for the pure resin (0% DDGS) case. The properties of pure resin were the arithmetic mean of two test specimens. (These runs were used to estimate the level of repeatability, which was approximately  $\pm 15\%$ .) This ratio is thus a direct measure of the mechanical property reduction (or potential enhancement) as DDGS is added at greater inclusion levels. These data are shown in Fig. 3, which plots the property ratios as a function of DDGS concentration. These results indicate a general downward trend in mechanical properties, as expected. However, for DDGS concentrations up to 50%, the property decrease was only 20–40%; in fact the Young's modulus at low DDGS content appears to be unchanged, which indicates that DDGS may provide

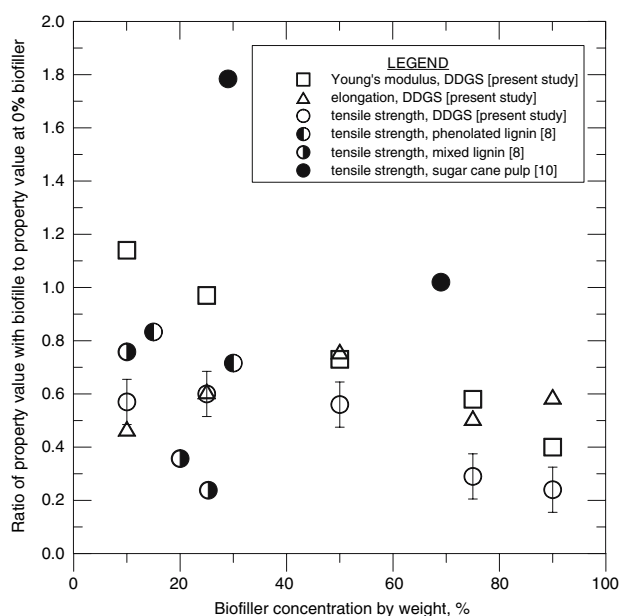
some stiffness to the material matrix. At DDGS inclusion greater than 75–90%, mechanical tensile strength was reduced by over 70%, and stiffness by about 50%. Although error bars ( $\pm 15\%$ ) are only displayed for the yield strengths, similar ranges of uncertainty are present for the Young's modulus and elongation ratios.

Figure 3 also provides results from some other studies for comparison purposes. It should be noted that direct data comparison is difficult, due to varying molding conditions, blends, and lack of pure resin data in many studies. Without pure resin data, the relative effects of adding biofiller cannot be ascertained with great certainty. Generally, tensile strength ratios from this study were less when compared to phenolated lignin formulations but were better than mixed lignin blends [8]. Sugar cane biofiller strength ratios were significantly greater than our DDGS-based composites; but, as already discussed, the pure phenolic matrix was not very strong initially [10]. Overall, DDGS appears to be competitive with other fillers. Follow-up studies will aim to more definitively quantify just how competitive DDGS is as a biofiller, and how best to utilize it as such.

## Conclusions

The goal of this study was to demonstrate the viability of using corn-based DDGS as a biofiller with phenolic resin to produce a novel biomaterial. It appears that filler concentrations between 25% and 50% represent reasonable inclusion values, as sufficient mechanical strength was retained, and DDGS replaced a proportionally greater quantity of resin. Resulting data were in the range of other studies that focused on biofillers, and procedures have been developed to successfully produce this unique composite. But only limited strength data have been reported here and follow-up studies should measure other mechanical and physical properties and quantify the effects of altering molding parameters, including molding pressure, temperature, and time, as well as DDGS content. It may be beneficial to treat the DDGS by drying or fractionation prior to molding. Additionally, strength of the DDGS composites should be optimized through the use of coupling agents or other additives. Development and characterization of these materials will provide data that are essential for the design of equipment and processing facilities, as well as optimization of subsequent unit operations in production settings, including compression molding.

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**Fig. 3** Comparison of mechanical properties, as a function of biofiller concentration, in phenolic resin-based composites

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